

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01D 53/86, B01J 23/889	A1	(11) International Publication Number: WO 00/25901 (43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/US99/19967 (22) International Filing Date: 31 August 1999 (31.08.99) (30) Priority Data: 98119648 3 November 1998 (03.11.98) RU 09/275,334 24 March 1999 (24.03.99) US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventors: DYCKMAN, Arkady Samuilovich; Raevskogo pr. 12, 42, St.Petersburg, 194064 (RU). FULMER, John, William; 78 Park Ridge Drive, Mt. Vernon, IN 47620 (US). PASTOR, Vladimir Yevgenyevich; Flat 2, Dimitrova ulitsa, 10-1, St.Petersburg, 192239 (RU). ZINENKOV, Andrey; Gagarina pr. 14/5, 103, St.Peterburg, 194064 (RU). (74) Agents: SNYDER, Bernard et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).		(81) Designated States: BR, CA, CN, IN, JP, KR, MX, RU, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL; PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR LOW TEMPERATURE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM INDUSTRIAL EXHAUST GAS (57) Abstract An efficient and effective process substantially reduces volatile organic compounds in a gaseous stream without the formation of nitrogen oxides and with low energy consumption. The process uses a bed of catalyst comprising manganese dioxide, copper oxide and potassium oxide. The gaseous stream containing volatile organic compounds passes through the catalyst bed at a temperature of from about 50 to about 150 °C and reduces the level of volatile organic compounds in the gaseous stream by at least about 90 percent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

PROCESS FOR LOW TEMPERATURE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM INDUSTRIAL EXHAUST GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims rights of priority under 35 U.S.C. § 119 from Russian Patent Application No. N 98119648, filed November 3, 1998.

FEDERALLY SPONSORED RESEARCH

Not applicable.

BACKGROUND OF THE INVENTION

5 This invention provides a method to substantially reduce the content of volatile organic compounds (VOCs) in industrial exhaust gas to enable the processes generating these gases to comply with increasingly stringent limits required by environmental control regulations.

10 The basis for choosing an appropriate exhaust gas purification method will depend on the level of the impurities, which must be removed. If the impurities concentration in the gas to be purified is as high as from about 0.5 to about 1.0 %, an adiabatic oxidation process may be suitable because the oxidation reaction heat is sufficient to keep the reactor temperature in an acceptable operating range. If the impurities concentration is lower than 0.05%, an isothermic process is needed which will require additional heat

from a source outside the process. Such a process is described in U.S. patent 5,292,991 Cl. C07C 7/152, C07C 7/00, issued March 8, 1994. According to this process, hydrocarbons and oxygen-containing organics are oxidized at 600°C over platinum-palladium catalyst modified with zirconium and titanium. The
5 disadvantage of this process is the necessity to heat the gas stream to a high temperature and its use of noble metals as the catalyst.

There are known methods for oxidizing VOCs at low temperature (including room temperature) over the catalysts containing platinum, palladium, and other rare and precious metals in amount up to 22% (e.g. US
10 patent 5,009,872, Cl. B 01 D, issued April 23, 1991). In this case complete methanol conversion was guaranteed. The disadvantage of this process is the extremely high catalyst cost.

Industrial exhaust gas purification from oxygen-containing organics and hydrocarbons over hopcalite-type catalysts, containing active manganese
15 dioxide and copper oxide, are known too, as mentioned in U.S. patent 5,238,897 Cl. B 01 J 23/34, B 01 J 23/72, B 01 J 37/34, issued 24.08.1993, hopcalite catalyst modified with yttrium, lithium, and lanthanum in an amount of from 3 to 15% provides practically complete hydrocarbons and oxygen-containing compounds conversion (starting concentration 400 - 2000
20 ppm) at 250 - 400°C.

In U.S. patent 5,238,897 hopcalite is used as a generic term to identify at column 4, lines 58 to 60, a copper/manganese compound used in gas masks to convert carbon monoxide into carbon dioxide. However, Ozone Engineering uses "Hopcalite" as a trademark in its literature describing Hopcalite Catalyst-
25 H Grade with a composition being a mixture of manganese dioxide and copper oxide. Lee et al. in Catalytic Oxidation of Carbon Monoxide at Low Temperature over Pd-Cu Loaded Porous Supports state with reference to low temperature oxidation of CO that a "catalyst known as Hopcalite is also

commercially available for similar use, which is a mixture of SnO_2 , MnO_2 , CuO and other oxides, but being prone to deactivation by the presence of water vapor."

The method closest to the method of removal of VOCs from industrial exhaust gas of the current invention is the process described in U.S. patent 4,238,460, Cl. B 01 D, issued December 9, 1980. According to this method, passing of aliphatic and aromatic hydrocarbons and products of their incomplete oxidation, containing 1 to 10 carbon atoms (and CO) in an amount of from 25 to 300 ppm over hopcalite catalyst at 140 - 540°C provides practically complete purification of exhaust gas from dangerous compounds. The disadvantage of this method is the necessity to heat the gas stream to a high temperature. This is especially disadvantageous if there is a large-volume of exhaust gas with high nitrogen concentration from which the well-known noxious by-products of nitrogen oxides (NOX) that are extremely detrimental to the environment.

SUMMARY OF THE INVENTION

The process for reducing the level of volatile organic compounds in a gaseous stream of the present invention substantially eliminates this detrimental formation of nitrogen oxides by the purification processes of the prior art by preparing a bed of catalyst comprising manganese dioxide, copper oxide and potassium oxide and passing through the catalyst bed a gaseous stream containing volatile organic compounds at a temperature of from about 50 to about 150°C. whereby the level of volatile organic compounds in the gaseous stream is reduced by at least about 90 percent. Not only does the present process minimize or substantially eliminate the formation of nitrogen oxides, but also its low operating temperature range substantially reduces the energy consumption of process which in turn reduces the environmental impact of the process and favorably affects the

economics of its operation. When formation of NOX or energy efficiency is not an issue, the process of the present invention can be equally effective in VOCs removal from gaseous streams at temperatures as high as about 200 to about 250°C.

- 5 The term "industrial exhaust gas" is intended to be construed in its broadest sense and includes any gaseous stream containing VOCs regardless of the source of these streams. Typical industrial exhaust gases include, but are not limited to, fugitive emissions and gases from vents from chemical processes, polymerization processes, waste treatment operations, storage
10 vessels, power plants, warehouses, distillation towers, separators, paint booths, laboratory hoods, pilot plants, degreasing operations, paint stripping operations, synthetic fiber production and spinning, petroleum cracking, ore refining, hydrocarbon processing, mechanical assembly operations, paper mills, cloth preparation, livestock enclosures and the like.
- 15 Although the present process is useful generally for the removal of any VOCs, VOCs that are removed by the present process with particular efficiency include ethers, preferably ethers containing from two to eight carbons, more, preferably dimethylether, diethylether and methylethyl ether and still more preferably dimethyl ether, alcohols, preferably alcohols
20 containing from one to four carbons, more preferably, ethanol and methanol, aldehydes, preferably aldehydes with from one to nine carbons, more preferably aldehydes with from one to seven carbons and still more preferably formaldehyde and acetaldehyde, ketones, preferably ketones with from three to nine carbons, more preferably ketones with from three to seven
25 carbons and still more preferably acetone and methylethyl ketone and esters, preferably esters with from three to nine carbons, more preferably esters with from three to seven carbons and still more preferably ethyl acetate and propyl acetate.

The industrial waste gas streams purified by the method of this invention include any streams in which VOCs occur at low levels, e.g., no more than about 1000 ppm, preferably from about 20 to about 500 ppm, more preferably from about 80 to about 400 ppm, still more preferably from about 150 to about 250 ppm and most preferably about 200 ppm. Industrial waste streams in which the method of this invention is preferably useful are waste streams from processes synthesizing organic compositions, more preferably waste streams from processes synthesizing oxygen-containing aromatic compounds and still more preferably waste streams from processes for synthesizing phenol.

DESCRIPTION OF THE DRAWINGS

Not applicable.

DETAILED DESCRIPTION OF THE INVENTION

The current invention surprisingly increases the activity of a manganese containing catalyst, such as a hopcalite catalyst, in exhaust gas purification to remove a high percentage, e.g., at least about 90%, preferably at least about 93%, more preferably at least about 96% and still more preferably at least about 98% of the VOCs present at low levels in the industrial waste gas stream at substantially lower temperatures without NOX formation. In a preferred embodiment, the present invention purifies waste streams contaminated with hydrocarbons by removing a high percentage, e.g., at least about 90%, preferably at least about 93%, more preferably at least about 96% and still more preferably at least about 98% of the hydrocarbon VOCs present at low levels in the industrial waste gas stream at substantially lower temperatures by the substantially complete conversion to more highly oxygenated organic compounds which, preferably, in turn, may be further oxidized to water and carbon dioxide.

A preferred manganese oxide/copper oxide catalyst which is a hopcalite type catalyst is commercially available from Carus Chemical Company under the trademark, CARULITE®, grade numbers 100, 110, 150, 200 and 300. and has a composition of about the following, as published in the trade literature:

50 - 75% MnO₂

10 - 40% CuO

10 - 20% Alumina binder (bentonite).

Some catalyst useful in the present process have compositions within this range as follows:

MnO ₂	CuO	Aluminum oxide
54%	36%	10%
60 - 75%	11 - 14%	15 - 16%

Other manganese-containing catalysts useful in the process of the present invention have been described as having an elemental manganese content of from about 37 - 39 % elemental manganese and an elemental copper content of about 9 - 11 % elemental copper.

The efficient and effective removal of VOCs from gaseous streams at low temperatures without substantial formation of NOX and with low energy consumption is accomplished by adding to the manganese-containing catalyst potassium oxide in amount of from about 0.01 to about 5% by weight, preferably from about 0.02 to about 4% by weight, more preferably from about 0.04 to about 3% by weight and still more preferably from about 0.05 to about 2.0% by weight of the catalyst, passing a gas stream, containing VOCs, over the manganese-containing catalyst containing the potassium oxide, at a

temperature of from about 50 to about 135°C, preferably from about 70 to about 135°C, more preferably from about 90 to about 130°C and still more preferably from about 100°C to about 130°C and at a space velocity of from about 2000 to about 15000 h⁻¹. Potassium oxide can be added to the catalyst composition in a stage of paste preparation by a known method (RF patent 2,064,834, Cl B 01 J 23/889, B 01 J 37/04), or with the feed compounds, used in catalyst production.

Although the space velocity of the gaseous stream is not critical to the practice of the process of the present invention so long as there is adequate contact with the catalyst bed which can be in the form of either a fixed bed or fluidized bed, it is preferred that the space velocity be within the range of from about 1000 to about 20000h⁻¹, more preferably from about 2000 to about 5000h⁻¹.

The catalyst can be employed in the present process without a support or supported. A preferred support is alumina.

In a preferred embodiment in which extended catalyst life is important to the practice of the invention, it has been found that by feeding to the catalyst bed a gaseous stream either added to the waste stream or separately oxygen at a volume percent of from about 2% to about 21% (the level of oxygen present in air), more preferably from about 4% to about 21% and still more preferably about 5% to about 21%, and operating the purification process at least about 100°C., catalyst life can be extended. Atmospheric air is the most convenient source of oxygen. It is postulated that at a temperature of 100°C. or greater, in the presence of the foregoing levels of oxygen the manganese monoxide is regenerated to the catalytically active species of manganese dioxide in the presence of the cupric oxide, the other essential component of the catalyst.

When operating the process of the present invention in the lower portion of the operating temperature range, i.e., from about 50°C. up to less than about 100°C., it is preferable to employ two catalyst beds in the practice of the present process, allowing one to be in use while the other is being regenerated. When operating the present process at about 100°C. or above, only one catalyst bed is required in view of the self-regeneration of the bed as described above. A second benefit of operating the present process at about 100°C. or above is the fact that at these operating temperatures any water present or formed in the removal of VOCs is present only as vapor. The water vapor rapidly exists the catalyst bed before it coats the active catalyst sites and deactivates the catalyst as taught in the prior art patent US 5,238,897.

The application of this invention is illustrated by the following examples but is not intended to be limited thereby. Percentages herein are expressed as weight percent unless expressly stated otherwise.

EXAMPLE 1

A glass reactor of 2.26 cm² cross-sectional area is filled with hopcalite catalyst, containing 0.05% potassium oxide. The catalyst particle size is from about 1 to about 3 mm. The catalyst bed depth is about 19 cm. The reactor is heated by an electric jacket to 95±1°C. Gas is fed as a stream at a rate through the reactor of about 46 l/h. The incoming gas composition is as follows (vol.%): nitrogen 91.0, oxygen 6.0, water as steam 3.0, methanol 0.02. Space velocity is 2000 h⁻¹ and linear velocity is about 0.9 m/sec. Experiment time is 4 hours. Total methanol amount entering in the incoming gas and passing through the catalyst bed in the reactor is 0.049 g. The gas exiting the reactor then passes through an absorption system, which consists of four concurrent traps (absorbers) cooled with a dry ice/acetone mixture (at a temperature of from -70 to -80°C). The first and last traps are empty. The second and third are filled with n-butanol. After the experiment finished, total methanol amount

found in traps is 0.00083 g, i.e. methanol conversion 98.3%. The methanol concentration in the gas stream is reduced from 200 ppm to 3.3 ppm.

EXAMPLE 2

The glass reactor, described in Example 1 is filled with 23 ml of
5 hopcalite catalyst, containing 2.0% potassium oxide. The catalyst bed temperature is $130\pm 1^\circ\text{C}$. The gas stream has the same composition as in Example 1 and passes through the reactor at a rate of 345 l/h, a space velocity of 15000 h^{-1} . In a period of 4-hours, the total methanol amount passed through the catalyst bed in the reactor was 0.368 g. The methanol amount collected in
10 the traps described in Example 1 was 0.00074 g, i.e., methanol conversion 99.8%. The methanol concentration in the gas stream was reduced from 200 ppm to 0.4 ppm.

EXAMPLE 3

The glass reactor, described in Example 1, is filled with 23 ml of
15 hopcalite catalyst, containing 0.5% potassium oxide. The catalyst bed temperature is $100\pm 1^\circ\text{C}$. A gas stream of the same composition as in Example 1 passes through the reactor at rate of 115 l/h, space velocity 5000 h^{-1} . In a period of 4-hours, the total amount of methanol passed through the catalyst bed in the reactor was 0.123 g. The methanol amount collected in the traps
20 described in Example 1 was 0.00012 g, conversion 99.9%. The methanol concentration in the gas stream was reduced from 200 ppm to 0.2 ppm.

EXAMPLE 4

The glass reactor, described in Example 1, was filled with 23 ml of hopcalite catalyst, containing 0.05% potassium oxide. The catalyst bed
25 temperature was $130\pm 1^\circ\text{C}$. A gas stream of a composition as indicated in Example 1, except for 0.02% of ethanol instead of methanol, is passed through

the reactor at a rate of 230 l/h, space velocity 10000 h⁻¹. In a period of 4-hours, the total ethanol amount passed through the catalyst bed in the reactor was 0.353 g. The ethanol amount collected in the traps described in Example 1 was 0.00106 g, conversion 99.7%. The ethanol concentration in the gas stream was
5 reduced from 200 ppm to 0.6 ppm.

EXAMPLE 5

The glass reactor described in Example 1 was filled with 23 ml of hopcalite catalyst, containing 2.0% potassium oxide. Catalyst bed temperature was 95±1°C. The gas stream had the same composition as indicated in
10 Example 1, except for 0.02% of ethanol instead of methanol, and was passed through the reactor at a rate of 46 l/h, space velocity 2000 h⁻¹. In the traps described in Example 1 was 0.00099 g, conversion 98.6%. The ethanol concentration in the gas stream was reduced from 200 ppm to 2.8 ppm.

The data from Examples 1 through 5 are summarized in the table below:

##	Organic impurity	K ₂ O in catalyst , %	Reaction temperature, °C	Space velocity, h ⁻¹	Impurity remainder, ppm	Impurity conversion , %
1	methanol	0.05	95	2000	3.3	98.3
2	methanol	2.0	130	15000	0.4	99.8
3	methanol	0.5	100	5000	0.2	99.9
4	ethanol	0.05	130	10000	0.6	99.7
5	ethanol	2.0	95	2000	2.8	98.6

EXAMPLE 6

To a glass reactor of 2.26 cm² cross-sectional area, 26 milliliters of hopcalite catalyst is added, containing 0.5% potassium oxide. The catalyst particle size is from about 1 to about 3 mm. The catalyst bed depth is about 19 cm. The reactor is heated by an electric jacket to 50±1°C. Gas is fed as a stream at a rate through the reactor of about 60 l/h. The incoming gas composition is as follows (vol. %): nitrogen 91.0, oxygen 6.0, water 3.0, methanol 0.02, cumene <10 ppm. Space velocity is 2400 h⁻¹. Residence time is 1.5 seconds. Pressure is about 1 atmosphere. The level of methanol is reduced by about 90% by volume.

EXAMPLE 7

To a glass reactor of 2.26 cm² cross-sectional area, 26 milliliters of hopcalite catalyst is added, containing 0.5% potassium oxide. The catalyst particle size is from about 1 to about 3 mm. The catalyst bed depth is about 19 cm. The reactor is heated by an electric jacket to 70±1°C. Gas is fed as a stream at a rate through the reactor of about 60 l/h. The incoming gas composition is as follows (vol.%): nitrogen 91.0, oxygen 6.0, water 3.0, methanol 0.02, cumene <10 ppm. Space velocity is 2400 h⁻¹. Residence time is 1.5 seconds. Pressure is about 1 atmosphere. The level of methanol is reduced by about 95% by volume.

COMPARATIVE EXAMPLE 1

Repeating the process substantially as described in Example 1 without the addition of potassium oxide and at each of the catalyst mid-bed temperatures as set forth below the percent removal of methanol is shown:

15	Catalyst Mid-Bed	Percent Methanol
	Temperature in °C.	Removal
	125	71
	140	81
	175	89
	200	96
20	235	99

This illustrates that without the addition of potassium oxide, a temperature of over 175°C. is required if it is desired to remove at least 90% of the methanol.

COMPARATIVE EXAMPLE 2

- Repeating the process substantially as described in Example 4 using
- 5 CARULITE 150 bead type hopcalite catalyst without the addition of potassium oxide a catalyst temperature of 167°C is required to remove 95% of the ethanol.

COMPARATIVE EXAMPLE 3

- Repeating the process substantially as described in Comparative
- 10 Example 2 but substituting for the ethanol the VOCs set forth below, the catalyst mid-bed temperatures to remove 95% of the VOCs are set forth below,

	Catalyst Mid-Bed Temperature in °C.	Oxygen-Containing Impurity
15	178	Propanol
	186	Methylethyl Ketone
	181	Ethyl Acetate
	200	Propyl Acetate
	278	Heptane
20	222	Toluene

COMPARATIVE EXAMPLE 4

Repeating the process substantially as described in Example 4 using CARULITE 110TR bead type hopcalite catalyst without the addition of potassium oxide a catalyst temperature of 222°C is required to remove 95% of the ethanol.

COMPARATIVE EXAMPLE 5

- 5 Repeating the process substantially as described in Comparative Example 4 but substituting for the ethanol the VOCs set forth below, the catalyst mid-bed temperatures to remove 95% of the VOCs are set forth below,

	Catalyst Mid-Bed	Oxygen-Containing
10	Temperature in °C.	Impurity
	250	Propanol
	<222	Methylethyl Ketone
	250	Ethyl Acetate
	222	Propyl Acetate
15	306	Heptane
	333	Toluene

EXAMPLE 8

Repeating the process substantially as described in Example 3 but substituting in the gas stream an equal amount of acetone for the methanol, the level of acetone was reduced to 18 ppm, a reduction of 91%.

EXAMPLE 9

Repeating the process substantially as described in Example 3 but substituting an equal amount of methylethyl ketone for the methanol, the level of methylethyl ketone was reduced to 15 ppm, a reduction of 92.5%.

EXAMPLE 10

A glass reactor, as described in Example 1, is filled with 23 ml of manganese oxide-containing catalyst, containing 1.0% potassium oxide. The catalyst bed temperature is $110 \pm 1^\circ\text{C}$. A gas stream of the composition of Example 1, except that 0.02%(vol.) of acetaldehyde is present in place of the methanol, is passed through the reactor at a rate of 115 l/h and a space velocity of 5000 h^{-1} . In a period of 4-hours, the total acetaldehyde amount passed through the catalyst bed is 0.169 g. The amount of acetaldehyde collected in traps is 0.00034 g, a reduction in acetaldehyde content of 99.8%. The acetaldehyde concentration in the gas stream is reduced from 200 ppm to 0.4 ppm.

CLAIMS:

What is claimed:

1. A process for the reduction of volatile organic compounds in a gaseous stream comprising preparing a bed of catalyst comprising manganese dioxide, copper oxide and potassium oxide and passing through the catalyst bed a gaseous stream containing volatile organic compounds at a temperature of from about 50 to about 150°C whereby the level of volatile organic compounds in the gaseous stream is reduced by at least about 90 percent.
2. The process of claim 1 wherein the potassium oxide is present in an amount of from about 0.01 percent to about 5 percent by weight of the catalyst.
3. The process of claim 1 wherein the potassium oxide is present in an amount of from about 0.02 percent to about 4 percent by weight of the catalyst.
4. The process of claim 1 wherein the potassium oxide is present in an amount of from about 0.04 percent to about 3 percent by weight of the catalyst.
5. The process of claim 1 wherein the potassium oxide is present in an amount of from about 0.05 percent to about 2 percent by weight of the catalyst.
6. The process of claim 1 wherein the level of volatile organic compounds in the gaseous stream is reduced by at least about 95 percent.
7. The process of claim 1 wherein the temperature of the gaseous stream in the catalyst bed is from about 70 to about 135°C.

8. The process of claim 1 wherein the temperature of the gaseous stream in the catalyst bed is from about 90 to about 130°C.
9. The process of claim 1 wherein the temperature of the gaseous stream in the catalyst bed is from about 100 to about 130°C.
- 5 10. The process of claim 9 wherein the gaseous stream is an industrial exhaust gas.
11. The process of claim 10 wherein only a single catalyst bed is employed.
12. The process of claim 1 wherein the catalyst is supported.
- 10 13. The process of claim 12 wherein the support is alumina.
14. The process of claim 1 wherein the catalyst is unsupported.
15. The process of claim 1 wherein the catalyst bed is a fixed bed.
16. The process of claim 1 wherein the catalyst bed is a fluidized bed.
- 15 17. The process of claim 1 wherein the catalyst contains from about 50 to about 75% manganese dioxide.
18. The process of claim 17 wherein the catalyst is a hopcalite catalyst.

19. A process for the reduction of volatile organic compounds in a gaseous stream comprising preparing a bed of catalyst comprising a hopcalite catalyst containing from about 50 to about 75% manganese dioxide by weight of the catalyst and passing through the catalyst bed a gaseous stream containing volatile organic compounds at a temperature of from about 50 to about 250°C whereby the level of volatile organic compounds in the gaseous stream is reduced by at least about 90%.

20. A process for the reduction of methanol or ethanol in a gaseous stream comprising preparing a bed of catalyst comprising a hopcalite catalyst containing from about 50 to about 75% manganese dioxide and potassium oxide in an amount of from about 0.05 percent to about 2 percent by weight of the catalyst and passing through the catalyst bed a gaseous stream containing methanol or ethanol at a space velocity of from about 1000 to about 20000h⁻¹ at a temperature of from about 100 to about 130°C whereby the level of methanol or ethanol in the gaseous stream is reduced by at least about 90%.

INTERNATIONAL SEARCH REPORT

Inter- national Application No

PCT/US 99/19967

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/86 B01J23/889

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D B01J A62D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 625 368 A (JAPAN PIONICS) 23 November 1994 (1994-11-23) page 2, line 51 -page 3, line 48 page 3, line 56 -page 4, line 3 page 4, line 26 - line 29 ---	1-18
A	FR 2 640 889 A (TOULOUSE INST NAT POLYTECH) 29 June 1990 (1990-06-29) page 2, line 19 -page 3, line 9 page 3, line 21 - line 36 page 4, line 9 - line 21; claims 1-13 --- -/--	1-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

12 January 2000

Date of mailing of the international search report

21/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

Inter. .nal Application No

PCT/US 99/19967

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 93 05879 A (NORTH CAROLINA CENTER FOR SCIE) 1 April 1993 (1993-04-01)</p> <p>page 1, line 33 -page 2, line 6</p> <p>page 3, line 33 -page 4, line 12</p> <p>page 7, line 1 -page 9, line 26</p> <p>page 10, line 25 -page 11, line 10</p> <p>page 13, line 4 - line 19</p> <p>page 15, line 24 -page 16, line 22</p> <p>-----</p>	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/19967

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0625368 A	23-11-1994	JP 6327932 A DE 69409423 D DE 69409423 T US 5512262 A	29-11-1994 14-05-1998 06-08-1998 30-04-1996
FR 2640889 A	29-06-1990	NONE	
WO 9305879 A	01-04-1993	US 5238897 A EP 0605633 A MX 9205478 A	24-08-1993 13-07-1994 01-08-1993